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IN RE APPLICATION OF:	:	
SATOSHI NIIYAMA, ET AL	:	GROUP ART UNIT: 1756
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FOR: LIQUID CRYSTAL OPTICAL ELEMENT AND METHOD FOR ITS PRODUCTION	:	

DECLARATION

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SIR:

Now comes MASAYUKI KUWANO who deposes and says:

That my name is MASAYUKI KUWANO ;

That my address is 5-24-310, 3-chome, Nakamachi, Musashino-shi, Tokyo, Japan;

That I know well both the English and Japanese languages;

That the attached English language translation is true and correct translation of Japanese Patent Application No JP10/298621 filed on October 20, 1998 to the best of my knowledge and belief.

I hereby declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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October 3, 2003
Date

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Applicant: Asahi Glass Company, Limited

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【Title of the Invention】

METHOD FOR PRODUCING LIQUID CRYSTAL OPTICAL ELEMENT

【Number of Inventions Stated in Claim(s)】 4

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【TYPE OF DOCUMENT】 SPECIFICATION

【TITLE OF THE INVENTION】

METHOD FOR PRODUCING LIQUID CRYSTAL OPTICAL ELEMENT

【SCOPE OF THE CLAIM(S)】

【Claim 1】

A method for producing a liquid crystal optical element, which comprises sandwiching a mixture of a liquid crystal with an uncured curable compound between a pair of substrates which are provided with transparent electrodes and of which at least one is transparent, and curing the curable compound to form a liquid crystal/cured composite layer, wherein the mixture contains a chiral agent, and the helical pitch of the chiral agent is at least 4 μm and at most three times of the electrode gap.

【Claim 2】

The method for producing a liquid crystal optical element according to Claim 1, wherein the electrode gap is from 4 to 50 μm.

【Claim 3】

The method for producing a liquid crystal optical element according to Claim 1 or 2, wherein the mixture contains a very small amount of a curing catalyst.

【Claim 4】

The method for producing a liquid crystal optical element according to Claim 1, 2 or 3, wherein the helical

pitch is at least 5 μm and at most two times of the electrode gap.

【DETAILED DESCRIPTION OF THE INVENTION】

【Technical Field to which the Invention Belongs】

The present invention relates to a liquid crystal optical element whereby the transmittance, scattering and reflection state of the element is controlled by application/non-application of an electric field and which is useful for e.g. a light-controlling element, a display element or an optical shutter.

【Prior Art】

A transmission/scattering type optical element has been proposed in which a liquid crystal and a transparent polymer are combined to form a difference in the refractive index between the polymer and the liquid crystal or in the interior of the liquid crystal (among microscopic regions). It is called, for example, a liquid crystal/polymer composite element, a liquid crystal/resin composite element or a dispersion type liquid crystal element. In principle, this element requires no polarizing plate, whereby the light absorption loss is small, and a high scattering performance can be obtained, and thus, it has a significant merit in that the light-utilizing efficiency in the entire element is high.

By utilizing such characteristics, it is employed for a light-controlling glass, an optical shutter, a

laser apparatus and a display apparatus. One showing a scattering state under application of no voltage and a transparent state under application of a voltage, has been commercialized.

Further, prior art reference 1 (USP 5,188,760) discloses an element employing a liquid crystal and a polymerizable liquid crystal. According to this prior art reference 1, under application of no voltage, the element shows a transparent state as observed from any direction as the liquid crystal and the polymerized liquid crystals in the element have the same alignment direction, and under application of a voltage, the alignment of the liquid crystals in the element is controlled by an electric field, and the alignment direction of liquid crystal molecules changes variously in the microscopic regions, whereby the element shows a scattering state.

Further, it has been disclosed that the contrast ratio can be improved by adding a chiral agent to provide a helical structure in the initial alignment. This element is called "an anisotropic gel" or "a liquid crystal gel". In this prior art reference 1, a mesogen monomer having acryloyl groups at the terminals was used.

Further, prior art reference 2 (PCT International Publication WO92/19695) also discloses an element having a similar structure. The operation mode was the same as in prior art reference 1, and a very small amount of a

polymer is dispersed in the chiral nematic liquid crystal to obtain a transparent state under application of no voltage and a scattering state under application of a voltage. This element is called PSCT (polymer stabilized cholesteric texture). Also in this prior art reference 2, a mesogen monomer having acryloyl groups at the terminals, was disclosed.

【Problems that the Invention is to Solve】

In the prior art, as a means to improve the contrast ratio in the transmittance (or the reflectance) of a liquid crystal optical element obtainable between application and non-application of a voltage, prior art reference 1 proposes to add a chiral agent to the mixture and to introduce a helical structure to the alignment mode of the curable compound after the curing.

Prior art reference 2 proposes to add a chiral agent to bring the helical pitch to a level of from 0.5 to 4 μm.

However, the addition of the chiral agent may sometimes cause a problem such that it increases the driving voltage of the element or it decreases the transmittance when the element is transparent. Further, when a mixture of a liquid crystal with an uncured curable compound, is injected into a liquid crystal cell, or when it is sandwiched between substrates provided with transparent electrodes, such as resin films provided with electrodes, if the chiral agent is contained in a large

amount, there will be a problem that injection irregularities or sandwiching irregularities are likely to result.

It is an object of the present invention to minimize the addition of the chiral agent and obtain a high contrast ratio in the transmittance characteristics obtainable at the time of application and non-application of a voltage, and not to increase the driving voltage as far as possible.

Further, characteristics of the liquid crystal optical element obtainable by preliminarily preparing a mixture containing a liquid crystal and an uncured curable compound and curing the curable compound, substantially depend on the structure of the liquid crystal/cured composite layer. Particularly, when a chiral agent is incorporated into the liquid crystal of the liquid crystal/cured composite layer, namely, when the composite contains a helical structure attributable to the chiral agent contained therein, the influence of the helical pitch to opt-electric characteristics is substantial.

Accordingly, the present inventors have conducted detailed researches on the added amount of the chiral agent contained in the mixture of the liquid crystal and uncured curable compound and the pitch of the helical structure derived therefrom. And, they have found that a region in which both a high contrast ratio and a low

driving voltage can be accomplished, may exist, under conditions of a large helical pitch which had never been employed.

【Means of Solving the Problems】

Namely, the present invention provides a method for producing a liquid crystal optical element, which comprises sandwiching a mixture of a liquid crystal with an uncured curable compound between a pair of substrates which are provided with transparent electrodes and of which at least one is transparent, and curing the curable compound to form a liquid crystal/cured composite layer, wherein the mixture contains a chiral agent, and the helical pitch of the chiral agent is at least 4 μm and at most three times of the electrode gap.

Further, in the above production method, the curable compound preferably contains a compound of the formula (1):

【Ka 1】

$$A_1\text{-}(OR_1)_n\text{-}O\text{-}Z\text{-}O\text{-}(R_2O)_m\text{-}A_2 \qquad \text{Formula (1)}$$

wherein each of A_1 and A_2 which are independent of each other, is an acryloyl group, a methacryloyl group, a glycidyl group or an allyl group; each of R_1 and R_2 which are independent of each other, is a $C_{2\text{-}6}$ alkylene group; Z is a bivalent mesogen structure; and each of n and m which are independent of each other, is an integer of from 1 to 10.

【Mode of Carrying out the Invention】

In the present invention, by adjusting the helical pitch within the above range, excellent properties not obtainable by the prior art can be accomplished. If the helical pitch is smaller than 4 μm, there will be a problem that the transmittance at the time of no application of a voltage tends to be low, or the driving voltage will increase.

If the helical pitch is larger than three times of the gap between the pair of electrodes sandwiching the liquid crystal/resin composite, the transmittance under application of a voltage will be high, and the contrast ratio in the transmittance between application and non-application of a voltage, tends to be low.

Further, by adjusting the helical pitch to be larger than 5 μm and at least two times of the electrode gap, it will be possible to adjust the balance of the low driving voltage and the high contrast.

The curable sites (A_1, A_2) of the formula (1) may be any of the above-mentioned functional groups which are photo curable or heat curable usually in the presence of a curing catalyst. Among them, an acryloyl group or a methacryloyl group suitable for photo curing, is preferred, since the temperature for the curing can be controlled.

The carbon numbers of the oxyalkylene portions R_1 and R_2 of the formula (1) are preferably from 2 to 6 from the

viewpoint of the mobility. Further, an ethylene group having a carbon number of 2 and a propylene group having a carbon number of 3, are preferred.

As the mesogen structural portion (Z) of the formula (1), a bivalent polyphenylene having at least two 1,4-phenylene groups bonded, is preferred. Further, some of 1,4-phenylene groups in this polyphenylene group may be bivalent organic groups substituted by a 1,4-cyclohexylene group.

Some or all of the hydrogen atoms of such a polyphenylene group or a bivalent organic group may be substituted by a substituent such as a C_{1-2} alkyl group, a halogen atom, a carboxyl group or an alkoxycarbonyl group. Preferred Z is a biphenylene group having two 1,4-phenylene groups bonded (hereinafter referred to as a 4,4'-biphenylene group), a terphenylene group having three such phenylene groups bonded, and a bivalent organic groups having from 1 to 4 hydrogen atoms of such a group substituted by a C_{1-2} alkyl group, a fluorine atom, a chlorine atom or a carboxyl group. Most preferred Z is a 4,4'-biphenylene group having no substituent.

If n and m of the formula (1) are too large, the compatibility with the liquid crystal deteriorates, and each of them is from 1 to 10, further preferably from 1 to 4 taking into consideration the characteristics of the element after curing.

The mixture of a liquid crystal with an uncured curable compound, may contain a curing catalyst, and in the case of photo curing, a photo polymerization initiator which is commonly used for a photo curable resin may be employed such as a benzoin ether type, an acetophenone type or a phosphine oxide type.

In the case of thermosetting, a curing catalyst such as a peroxide type, a thiol type, an amine type or an acid anhydride type, may be used depending upon the type of the curable sites, and if necessary, a curing assistant such as an amine may also be used.

The content of the curing catalyst is preferably at most 20 wt% of the uncured curable compound contained, and in a case where a high molecular weight or a high resistivity is required for the cured product after curing, it is more preferably from 1 to 10 wt%.

In order to improve the compatibility with liquid crystal, the uncured curable compound in the mixture of liquid crystal with the curable compound, may contain a plurality of uncured curable compound differing in n and m in the formula (1), whereby the contrast may further be improved.

On the other hand, the mixture of a liquid crystal with an uncured curable compound, is preferably a homogeneous solution after mixing. Further, the mixture of a liquid crystal with an uncured curable compound may show a liquid crystal phase when sandwiched between the

substrates provided with electrodes.

Further, the mixture of a liquid crystal with an uncured curable compound, may show a liquid crystal phase when it is cured. It is also possible to impart a function to align the liquid crystal to the electrode surface by directly rubbing the electrode surface of the substrates provided with electrodes, which sandwich the mixture of a liquid crystal with an uncured curable compound, or by forming a thin film of a resin thereof and rubbing the thin film, whereby it is possible to reduce irregularities at the time of sandwiching the mixture of a liquid crystal and an uncured curable compound.

Further, the combination of the alignment directions of the pair of alignment-treated substrates may be parallel or orthogonal, and the angle may be set to make the irregularities be minimum at the time of sandwiching the mixture.

The distance between the electrodes may be maintained by e.g. a spacer, and the gap is preferably from 4 to 50 μm, more preferably from 5 to 30 μm. If the electrode gap is too small, the contrast tends to deteriorate, and if it is too large, the driving voltage will increase.

The substrates supporting electrodes, may be glass substrates or resin substrates, or a combination of a glass substrate and a resin substrate. Further, one side

may be a reflecting electrode made of an aluminum or dielectric multi-layer film.

In the case of film substrates, the productivity is high, because it is possible that continuously supplied substrates provided with electrodes, are sandwiched between pairs of rubber rolls, and a mixture of a liquid crystal and an uncured curable compound, having a spacer incorporated and dispersed therein, is sandwiched between them, followed by continuous curing.

In the case of glass substrates, a very small amount of a spacer is distributed inside of the electrode surfaces, and the four sides of the opposing substrates are sealed with a sealing agent such as an epoxy resin to form a sealed cell, and one of cutouts of the seal formed at two or more portions is dipped in a mixture of a liquid crystal with an uncured curable compound, and suctioning from the other to fill the mixture into the cell, followed by curing to obtain a liquid crystal optical element. Otherwise, a vacuum injection method may also be employed. Now, the present invention will be described in detail with reference to Examples.

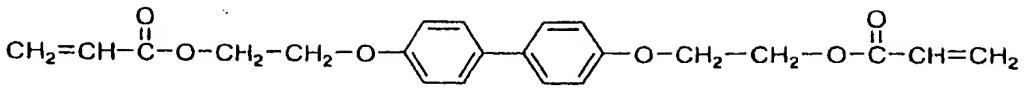
【Examples】

EXAMPLE 1

A mixture (mixture A) comprising 95 parts of a cyano type nematic liquid crystal (BL-006, manufactured by Merck), 5 parts of an uncured curable compound of the formula (2) and 0.15 part of benzoin isopropyl ether, was

prepared.

【Ka 2】



Formula (2)

This compound of the formula (2) corresponds to a compound of the formula (1) wherein A_1 and A_2 are each an acryloyl group, R_1 and R_2 are each an ethylene group, the mesogen structural portion of Z is a 4,4'-biphenylene group, and each of n and m is 1.

A mixture having 3.5 parts of a chiral agent (a mixture comprising S-811, manufactured by Merck and C15 manufactured by Merck in a weight ratio of 1:1, hereinafter referred to as chiral agent A) uniformly dissolved in 100 parts of mixture A, was prepared (mixture B). Then, it was injected into a wedge cell for measuring the helical pitch, and the pitch was measured, whereby the helical pitch was found to be 5.1 μm.

This mixture B was injected into a liquid crystal cell prepared by bonding a pair of substrates having thin polyimide films formed on transparent electrodes and rubbed in one direction, so that the rubbing directions crossed each other, via a very small amount of resin beads having a diameter of 13 μm, by an epoxy resin printed in a width of about 1 mm along the four sides.

While maintaining this liquid crystal cell at 25°C, ultraviolet rays of 3 mW/cm^2 from the upper side and

ultraviolet rays of about 3 mW/cm^2 from the lower side, were irradiated for 10 minutes by a HgXe lamp having a main wavelength of about 365 nm, to prepare a liquid crystal optical element.

An operation of applying a voltage of 50 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured by a transmittance measuring system (F value of the optical system: 11.5) employing a measuring light source having a center wavelength of 530 nm and a full width at half maximum value of about 20 nm, whereby the transmittance was 78% when no voltage was applied, and the value of a contrast ratio obtained by dividing this value by the transmittance when 50 Vrms was applied, was 23.

In a case where the transmittance of this liquid crystal optical element when no voltage was applied, was 100%, and the transmittance when a voltage of 50 Vrms was applied, was 0%, the applied voltage showing a transmittance of 50% i.e. a value (V_{50}) of the applied voltage showing a change of 50% in transmittance, was 23 Vrms.

EXAMPLE 2

A mixture having 1.5 parts of the chiral agent A of Example 1 uniformly dissolved in 100 parts of the mixture A of Example 1, was prepared (mixture C). In the same

manner as in Example 1, it was injected into a wedge cell for measuring the helical pitch, and the pitch was measured, whereby the helical pitch was 10.8 μm.

This mixture C was injected into a liquid crystal cell having the same structure as used in Example 1, and ultraviolet rays were irradiated in the same manner at 25°C to cure the uncured curable compound, to form a liquid crystal optical element.

An operation of applying a voltage of 50 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured by the same transmittance measuring system as in Example 1, whereby the transmittance was 81% when no voltage was applied, and the value of a contrast ratio obtained by dividing this value by the transmittance when 50 Vrms was applied, was 23, and V_{50} was 19 Vrms.

COMPARATIVE EXAMPLE 1

Without adding any chiral agent, mixture A of Example 1 was injected into a liquid crystal cell having the same structure as used in Example 1, and ultraviolet rays were irradiated in the same manner at 25°C to cure the uncured curable compound, to obtain a liquid crystal optical element.

In this liquid crystal cell, the alignment directions were crossed each other, whereby as injected into the cell, mixture A shows a helical pitch of about

four times of the distance between the electrodes of the cell, on appearance.

An operation of applying a voltage of 50 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured by the same transmittance measuring system as in Example 1, whereby the transmittance was 79% when no voltage was applied, and the value of a contrast ratio obtained by dividing this value by the transmittance when 50 Vrms was applied, was 3.2, and V_{50} was 18 Vrms.

COMPARATIVE EXAMPLE 2

A mixture having 7.5 parts of the chiral agent A of Example 1 uniformly dissolved in 100 parts of the mixture A of Example 1, was prepared (mixture D). In the same manner as in Example 1, it was injected into a wedge cell for measuring the helical pitch, and the pitch was measured, whereby the helical pitch was 2.4 μm.

This mixture D was injected into a liquid crystal cell having the same structure as used in Example 1, and ultraviolet rays were irradiated in the same manner at 25°C, to cure the uncured curable compound, to form a liquid crystal optical element.

An operation of applying a voltage of 50 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured

by the same transmittance measuring system as in Example 1, whereby the transmittance was 73% when no voltage was applied, and the value of a contrast ratio obtained by dividing this value by the transmittance when 50 Vrms was applied, was 13, and V_{50} was 31.

EXAMPLE 3

Two parts of a chiral agent (a mixture comprising R-811, manufactured by Merck and CB15 manufactured by Merck in a weight ratio of 1:1, hereinafter referred to as chiral agent B) was uniformly dissolved in 100 parts of mixture A of Example 1 to prepare a mixture (mixture E). Then, it was injected into a wedge cell for measuring the helical pitch, and the pitch was measured, whereby the helical pitch was found to be 5.7 μm.

This mixture E was injected into a liquid crystal cell having the same structure as used in Example 1, and ultraviolet rays were irradiated for one minute in the same manner as in Example 1 at 25°C to cure the uncured curable compound, to form a liquid crystal optical element.

An operation of applying a voltage of 50 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured by the same transmittance measuring system as in Example 1, whereby the transmittance was 81% when no voltage was applied, and the value of a contrast ratio obtained by

dividing this value by the transmittance when 50 Vrms was applied, was 31, and V_{50} was 22 Vrms.

EXAMPLE 4

0.5 Parts of the chiral agent B of Example 3 was uniformly dissolved in 100 parts of the mixture A of Example 1 to prepare a mixture (mixture F). In the same manner as in Example 1, it was injected into a wedge cell for measuring the helical pitch, and the pitch was measured, whereby the helical pitch was 21 μm.

This mixture F was injected into the same liquid crystal cell as used in Example 1, and ultraviolet rays were irradiated in the same manner as in Example 3 at 25°C, to cure the uncured curable compound, to obtain a liquid crystal optical element.

An operation of applying a voltage of 50 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured by the same transmittance measuring system as in Example 1, whereby the transmittance was 80% when no voltage was applied, and the value of a contrast ratio obtained by dividing this value by the transmittance when 50 Vrms was applied, was 14, and V_{50} was 17 Vrms.

COMPARATIVE EXAMPLE 3

Without adding chiral agent, mixture A of Example 1 was injected into a liquid crystal cell having the same structure as used in Example 1, and ultraviolet rays were

irradiated in the same manner as in Example 3 at 25°C, to cure the uncured curable compound, to obtain a liquid crystal optical element.

This liquid crystal cell was a cell in which the alignment directions crossed each other, whereby as injected into the cell, mixture A shows a helical pitch of about 4 times of the distance between electrodes of the cell, on appearance.

An operation of applying a voltage of 50 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured by the same transmittance measuring system as in Example 1, whereby the transmittance was 78% when no voltage was applied, and the value of a contrast ratio obtained by dividing this value by the transmittance when 50 Vrms was applied, was 3.9, and V_{50} was 10 Vrms.

COMPARATIVE EXAMPLE 4

Four parts of the chiral agent B of Example 3 was uniformly dissolved in 100 parts of the mixture A of Example 1 to prepare a mixture (mixture D). In the same manner as in Example 1, it was injected into a wedge cell for measuring the helical pitch, and the pitch was measured, whereby the helical pitch was 3.0 μm.

This mixture D was injected into the same liquid crystal cell as used in Example 1, and ultraviolet rays were irradiated in the same manner as in Example 3 at

25°C, to cure the uncured curable compound, to form a liquid crystal optical element.

An operation of applying a voltage of 50 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured by the same transmittance measuring system as in Example 1, whereby the transmittance was 79% when no voltage was applied, and the value of a contrast ratio obtained by dividing this value by the transmittance when 50 Vrms was applied, was 25, and V_{50} was 28 Vrms.

【Effects of the Invention】

The liquid crystal optical element of the present invention can be operated at a low driving voltage and the contrast ratio in transmittance between application and non-application of an electric field can be made high, and thus it is suitable for e.g. a light-controlling glass, an optical shutter, or a display for which the driving voltage is restricted.

Further, the transmittance of the element when it is transparent, can be made high, and irregularities in the transmittance derived from the injection step or the sandwiching step can be made small, whereby it is possible to provide a liquid crystal optical element suitable for e.g. a high quality light-controlling glass or optical shutter.

Further, the contrast ratio can be substantially

improved at a low voltage without substantially increasing the driving voltage, whereby it can be used for a display element.

【TYPE OF DOCUMENT】 ABSTRACT

【SUMMARY】

【OBJECT】

A method for producing a liquid crystal optical element which shows a high contrast ratio and can be operated at a low driving voltage.

【MEANS OF SOLVING PROBLEMS】

A method for producing a liquid crystal optical element, which comprises sandwiching a mixture of a liquid crystal with an uncured curable compound between a pair of substrates which are provided with transparent electrodes and of which at least one is transparent, and curing the curable compound to form a liquid crystal/cured composite layer, wherein the mixture contains a chiral agent, and the helical pitch of the chiral agent is at least 4 μm and at most three times of the electrode gap.

【SELECTED FIGURE】 No Selected Figure